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INDUCTION OF OLEFIN METATHESIS BY PHENYLACETYLENE PLUS TUNGSTEN--ETC(U)
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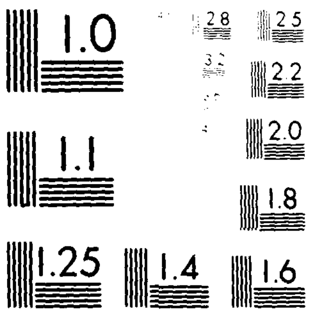

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Phenylacetylene induces tungsten hexachloride to initiate metatheses of cis-2-pentene, cyclopentene, cycloheptene, and cyclooctene. In too large amounts, however, it is ineffective. The reactions are run in the atmosphere. The stereoselectivities for cis-olefins are moderate.

OFFICE OF NAVAL RESEARCH

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Induction of Olefin Metathesis by Phenylacetylene Plus Tungsten Hexachloride

by

Thomas J. Katz, Chien-Chung Han

Prepared for Publication

in

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June 21, 1982

The discovery by Masuda et al. that tungsten hexachloride initiates polymerization of phenylacetylene[1] suggests the following proposition: that phenylacetylene may effectively replace the highly reactive organo-aluminum component in the mixture with tungsten hexachloride that is the archetypical[2] and still standard initiator for olefin metathesis.[3] For if the metal-catalyzed polymerization of acetylenes is an olefin metathesis,[4-6] a metallic compound that induces an acetylene to polymerize should itself be induced by the acetylene to metathesize olefins. The idea was demonstrated recently with phenylacetylene plus (phenylmethoxycarbene)pentacarbonyltungsten.[6] It is shown here also for phenylacetylene plus tungsten hexachloride, a combination that is more available, acts faster, induces fair stereoselectivy, and can be used unprotected in the atmosphere.[7]

Fig 1 Figure 1 shows phenylacetylene's effect on the metathesis of cis-2-pentene[14] according to eq 1.[15] As phenylacetylene is added, the

$$\underset{200}{CH_3CH{=}CHC_2H_5} + \underset{1}{WCl_6} + \underset{x}{C_6H_5C{\equiv}CH} \quad (1)$$

$$\xrightarrow[\substack{30^\circ C \\ 70\ min}]{C_6H_5Cl} (CH_3CH\!\!\rightarrow_2 + (C_2H_5CH\!\!\rightarrow_2$$

amount of reaction, negligible in its absence, rises dramatically and then falls. Complete reaction is easily achieved, but only when the amount of acetylene is appropriate.

Table I Table I similarly shows phenylacetylene's ability to stimulate tungsten hexachloride to polymerize three cyclic olefins (eq 2), reactions that (as seen in the table) occur inappreciably, if at all, when

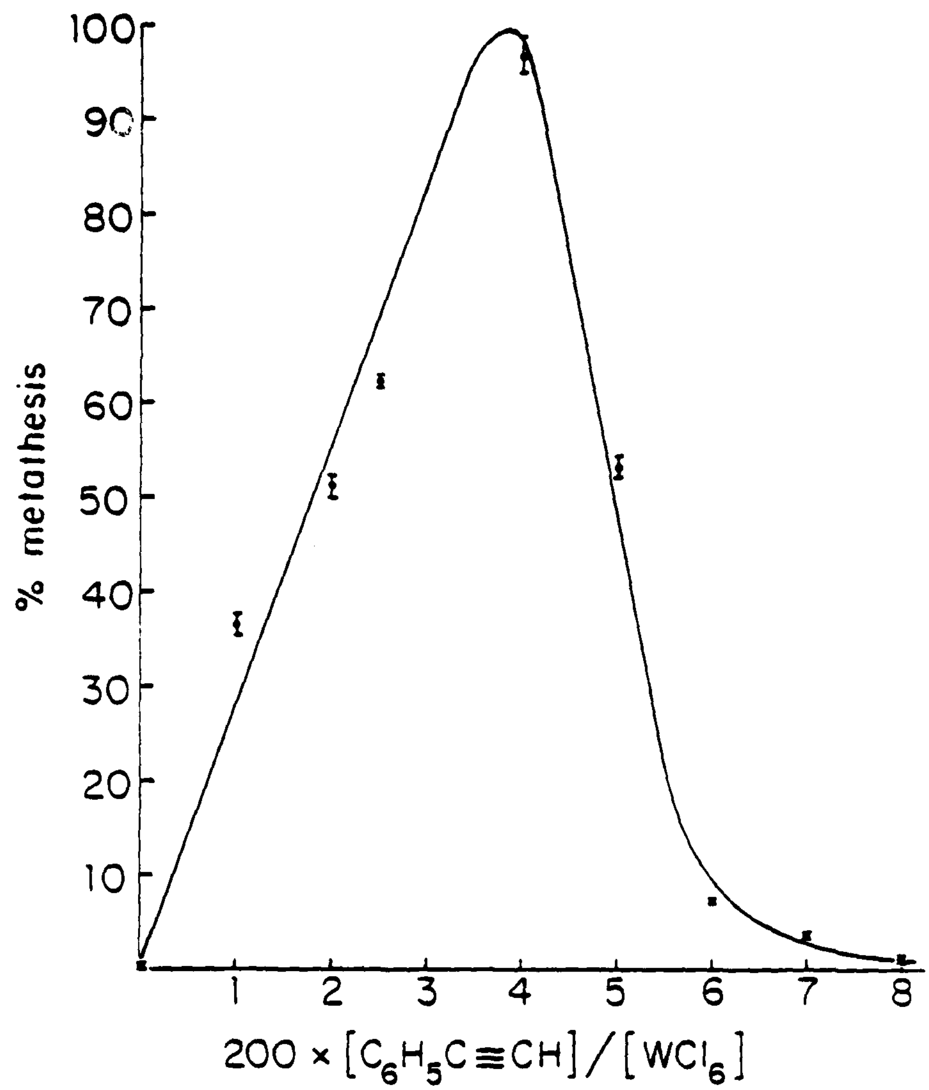
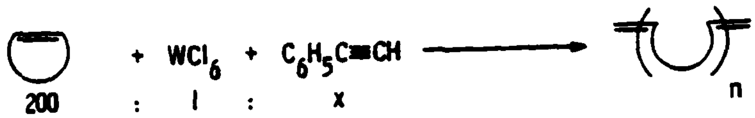


Figure 1. The extent of reaction according to eq 1 as a function of x. Precent metathesis is recorded as 200r/(1 + 2r), where r is the ratio in moles of either 2-butene to 2-pentene or 3-hexene to 2-pentene. The bars span the two values associated with r measured in the two ways.

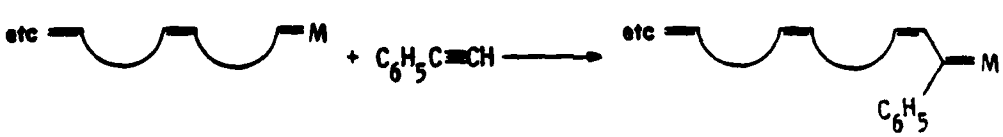


(2)

phenylacetylene is absent. That the polymers formed are indeed polyalkenamers, not saturated vinyl polymers, is attested to by their ^{1}H NMR spectra displaying only the required resonances and intensities. The latter measure contamination by saturated hydrocarbon amounting to no more than 4-9% (±4%).

Table II

Table II shows that for cyclopentene, as for 2-pentene, while small amounts of phenylacetylene induce metathesis, larger amounts quench reaction. The decreased molecular weights (also recorded there) when the amount of acetylene is large imply that growing chains rather than initiating centers are being extinguished. This termination may involve eq 3, the transformation of a simpler metal-carbene into one more highly substituted and with conjugating groups.[6b] One might speculate that the initiation involves eq 4, possibly accompanied by



(3)

$$-C\equiv C- + WCl_6 \longrightarrow -\underset{}{C}(WCl_5)=CCl- \longrightarrow -C(=WCl_4)-CCl_2- \qquad (4)$$

reaction with additional acetylene reducing the tungsten's oxidation state.[18]

A hypothesis associating diminished stereoselectivity with the presence of Lewis acids[3e,19] suggests that stereoselectivity should increase when an aluminum halide is replaced by phenylacetylene and decrease when (phenylmethoxycarbene)pentacarbonyltungsten is replaced by tungsten hexachloride. The stereoselectivities recorded in Table II and the stereochemistries of the 2-butenes (initially 69.6% cis) and 3-hexenes (initially ca. 54% cis) in Figure 1 accord with this hypothesis.[20]

Acknowledgments. We are grateful to the National Science Foundation (CHE-81-08998) and the U.S. Office of Naval Research for support.

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(7) Tungsten hexachloride alone does not metathesize olefins that are unstrained,[8] but it does metathesize examples that are strained (like norbornene and dicyclopentadiene).[10] Küpper demonstrated that combined with more reactive olefins it would induce the reactions of those that are less reactive,[11] and Makovetskii et al. very recently discovered results similar to some of those reported here, in which it is effective in combination with acetylenes.[12] Phenylacetylene is also recorded among additives that enhance the reactivity of tungsten hexachloride plus tetrabutyltin.[13]

(8) In the presence of oxygen, but not in its absence, WCl_6 is reported to polymerize cyclopentene to polypentenamer.[9] Similar, but not identical, experiments (see Table I) failed for us. After a long time (22 h) at 30 °C with WCl_6 in air in the absence of solvent, cyclopentene gave a 2.6% yield of polymer that was 80% saturated (^1H NMR analysis). In an equal volume of chlorobenzene (not toluene and not distilled from triethylaluminum) after the same amount of time it did not polymerize appreciably.

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(14) 99.6% cis, containing 0.25% n-pentane.

(15) The volume of chlorobenzene equalled that of the cis-2-pentene. No precaution was taken to exclude air.

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(20) See the results and summaries in references 3e, 6a, 16 , and 19. Küpper's aluminum-free catalysts induce stereochemistries like those here.[11] For cyclopentene's metathesis decreasing amounts of aluminum halides decrease the stereoselectivity,[21] and metals (like Sn[22] and Si[23]) whose halides are less acidic than aluminum's enhance stereoselectivity.

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Table I. Yields, Stereochemistries, and Molecular Weights of Polymers Prepared According to Equation 2 When x = 1, 4, or 0.[a]

cyclo-alkene[b]	Reaction temperature (°C)	Reaction time	x	Yield (%)[c]	% cis IR[d]	% cis ^{13}C NMR[e]	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$ [f]
5	24	320 s	1	9.8±1	61.1±2	40.1±2	155	89
5	24	320 s	0	0.065±0.02				
8	30	5 h	4	21.4±0.4	79.4±0.7	74.5±0.6		
8	30	5 h	0	0.3±0				
8	30	19 h	1	17.2±1	86.1±1	85.0±0.9	223	127
8	30	19 h	0	0.9±0.7				
7	30	24 h	1	57.6	73.3±0.7	67.9±2	[g]	
7	30	24 h	0	0.8				

[a] Cyclopentene and cyclooctene were diluted with equal volumes of chlorobenzene, but cycloheptene was not. Reactions were effected in the atmosphere. [b] The number of carbons in the cycloalkene. [c] After dissolving in methylene chloride, precipitating with methanol, washing with aqueous ammonia and methanol (not for cycloheptene), and vacuum drying. The average deviation listed is that of three experiments with cyclopentene and two with cyclooctene. [d] Measured by the IR spectra of thin films as described in footnote 16 of reference 1b. The average deviations are of 2-4 measurements. [e] Measured by the intensities of resonances near 32 and 27 ppm. Spectra were

acquired using $CDCl_3$ solutions, a 20 MHz spectrometer with proton noise decoupling and no relaxation delay (see note 17). [f]Measured by gel-permeation chromatography using tetrahydrofuran solutions, a refractive index monitor, and 5 Waters Associates μ-styragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å). The curves are bimodal (ref 6b), and it is the analyses of the high-molecular weight peaks that are recorded. The values recorded are half the weights of the polystyrenes that would exhibit the chromatograms observed (see Table II in ref 6a and Table I in ref 6b). [g]Not measured, but $[\eta] = 6.15 \pm 0.2$ dL/g in toluene at 29.7 °C.

Table II. The Dependence of the Yields and Molecular Weights of Polypentenamers Prepared According to Equation 2 (after 8 min at 21 °C) on the Amount of Phenylacetylene in the Reaction Mixture.[a]

x[b]	Yield (%)[c,d]	$\bar{M}_n$ 10^{-3} [e]
0	0.12	
0.31	3.6±3	33.5±7
1.25	5.6±4	143.6±5
2.5	16.8±4	79.1±0.2
3.75	14.9±3	22.5±0.3
7.5	(4.8)	15.2±0.02
10	(4.2)	

[a]Cyclopentene was diluted with an equal volume of chlorobenzene. Reactions were effected in the atmosphere. [b]The number of moles of phenylacetylene per 200 moles of cyclopentene. [c]100 x (weight of polymer/weight of cyclopentene + phenylacetylene). If the yield of polyphenylacetylene were 75% the yields of polypentenamer would (for $x \leq 3.75$) be 0.12, 3.4, 5.0, 15.8, and 13.4. For $x = 7.5$ and 10 however, much of the polymer is polyphenylacetylene, and if its yield were 75%, that of polypentenamer would be negligible. [d]Worked up as in Table I, note c. [e]See footnote f in Table I. The averages and standard deviations of measurements made using a refractive index monitor and a detector of light absorption at 400 nm. The figures on the last two lines were estimated by supposing that the single peaks observed could be dissected into two overlapping components.

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